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# Protection Level Afforded by the Canadian C7 Canister Against Single Large-Scale Release of Chlorine

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# DEFENCE RESEARCH ESTABLISHMENT SUFFIELD

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# PROTECTION LEVEL AFFORDED BY THE CANADIAN C7

# CANISTER AGAINST SINGLE LARGE-SCALE RELEASE OF CHLORINE

by

S.H.C. Liang, E.C. Yee and S.J. Armour

## ABSTRACT

The Canadian C7 canister was challenged at various concentrations of chlorine to determine the breakthrough times. During the breakthrough experiments, it was found that at chlorine concentration above 10,000 ppm, the canister underwent spontaneous ignition before breakthrough occurred. The CANSLAB dense gas model developed at DRES was used to calculate the peak mean concentration and total dosage as a function of downwind distance that can be expected from the catastrophic failure of chlorine cylinders and tank cars under the worst but feasible meteorological condition. Combining the CANSLAB calculations and the breakthrough results, distances downwind of the release site where the C7 canister will ignite (spontaneous ignition distance) or allow breakthrough of chlorine (breakthrough distance) were determined. From the combined result, it could be concluded that providing the wearer is beyond the spontaneous ignition distance, the C7 canister should provide the wearer with respiratory protection and to safely evacuate from an area contaminated with chlorine.

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## EXECUTIVE SUMMARY

### TITLE

Liang, S.H.C., Yee, E.C. and Armour, S.J. "Protection Level Afforded by the Canadian C7 Canister Against Single Large Scale Release of Chlorine" DRES SR-680, December 1997.

### INTRODUCTION

The Canadian Forces are equipped with the C4 mask and C7 canister for respiratory protection against the threat of chemical warfare (CW) agents. The C7 plastic canister is the first Western canister capable of providing protection against the full spectrum of CW agents. Since the C7 canister was developed for military use, chemical warfare agents were used in standard protection level determinations. It is well known that the C7 canister will also provide some protection against a variety of toxic industrial chemicals (TICs), such as hydrogen sulfide and chlorine. However, no detailed study has ever been undertaken to investigate the full extent of protection and the different scenarios where the C7 canister may be used against these toxic chemicals.

Although less toxic than CW agents, industrial chemicals are often available in enormous quantities and can be mass-produced easily. These chemicals could also be released from industrial plants or storage depots through battle damage, as a consequence of a strike against a particular facility, or as a desperate measure during military operations. To address the concern with TICs, DRES has recently initiated a program in evaluating the performance of the C7 canister against a variety of TICs.

### RESULTS

The breakthrough times of the C7 canister were measured at various concentrations of chlorine and at two humidities. It was found that the C7 canister provides quantitative protection against chlorine at low concentration, and that the protection is not humidity-related. At chlorine

concentration above 10000 ppm, the C7 canister underwent spontaneous ignition before breakthrough occurred. Thus, it appeared that there are two hazards for gas mask wearers in a chlorine environment: breakthrough of the gas mask at high dosage (concentration multiplied by time), and ignition of the canister at high concentration. However, this information means very little to the commander of the troops in the field. It was then decided to present the above numbers in a more comprehensive manner. The CANSLAB dense gas model developed at DRES was used to calculate the peak mean concentration and total dosage as a function of downwind distance that can be expected from the catastrophic failure of chlorine cylinders and tank cars under the worst but feasible meteorological condition. The CANSLAB calculations and the breakthrough results were combined. Distances downwind of the release site where the C7 canister will ignite (spontaneous ignition distance) or allow breakthrough of chlorine (breakthrough distance) were determined. From the combined result, it could be concluded that providing the wearer is beyond the spontaneous ignition distance, the C7 canister should permit the wearer to safely evacuate the area following the sudden release of chlorine without risk of breakthrough.

## SIGNIFICANCE OF RESULTS

It is known that C7 canister can provide protection against a variety of toxic industrial chemicals, in which chlorine is a typical example. However, it is not known that the canister will ignite at high concentration of chlorine gas.

The information reported here will allow the commander of the troops to estimate whether the C7 canister may be used effectively and safely in an environment contaminated with chlorine. This can be obtained from the estimated amount of chlorine released (e.g., the number of railway tanker cars which have been derailed and cracked open), and the distance the troops are stationed away from the site of chlorine release. There are times that valuable assets have to be protected and that self-contained breathing apparatuses are not readily available. The C4 mask and C7 canister ensemble may become the last line of defence. However, it should be pointed out that the respirator ensemble is designed for the purpose of escaping from a hazard area only.

## FUTURE GOALS

Chlorine gas is a typical industrial gas in the class of heavy gases (heavier than air). This study on the protection against TICs by the C7 canister will be extended to other gases including light gases (such as ammonia), and intermediate density gases (such as carbon monoxide). This will involve similar breakthrough studies while applying the appropriate CANSLAB light gas model.

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## 1.0    INTRODUCTION

The threat that combatants in the Bosnian civil war might use chlorine against NATO forces (which included units from Canada, the United Kingdom and the United States) highlighted the potential of toxic industrial chemicals (TICs) as weapons of opportunity. Although less lethal than chemical warfare nerve agents, industrial chemicals are often available in enormous quantities, are easily mass produced, and do not require extensive research programs. TICs have potential for inclusion in clandestine weapons programs and could prove, because of their availability, very attractive to terrorists. In addition, they could be released from industrial plants or storage depots through battle damage, as a consequence of a strike against a particular facility, or as a desperation measure during military operations.

To address the hazard from the use of TICs in Bosnia against NATO forces, the US/UK/CA Memorandum of Understanding on Chemical and Biological Defence (MOU on CBD) formed International Task Force-25 (ITF-25) on the Hazard from Toxic Industrial Chemicals [1] in March 1994. ITF-25 defined toxic industrial chemicals as those chemicals that are produced in quantities exceeding 30 tonnes per year at a single facility and have a $LCt_{50}$ value by inhalation in any mammalian species of less than 100,000 $mg.min.m^{-3}$. Eleven hundred sixty-four chemicals were identified which met the toxicity criterion. This number was reduced by considering only those chemicals that have an appreciable vapour pressure at $20°C$, or were listed in the U.S. Department of Transportation Emergency Response Guide. By applying the producibility criterion the number was further reduced to 98. A Hazard Index was developed to rank these 98 TICs according to their significance in a military situation. Twenty-one chemicals were ranked "high", 41 "medium" and 36 "low" (see Annex A). Chlorine was considered to present the greatest hazard.

ITF-25 concluded that, **"It is vitally important that commanders and troops be made aware that the best defence against toxic industrial chemical releases is to escape the path of the toxic chemical immediately. The respirator can provide limited protection and should only be used to escape the hazard area."** [1]

NATO subsequently issued an ACE Directive [2] that states, "Standard issue NBC filters have only been tested for their effectiveness against known chemical warfare agents. Military filters should not be relied upon for protection against TICs. The military respirator should only be used for emergency protection against the immediate effects of a toxic release while evacuating the immediate hazard zone. Both individual and vehicular collective filters may heat and burn when exposed to high concentrations of certain TICs"

ITF-25 and the NATO ACE Directive writers concluded that military respirators should only be used to evacuate the immediate hazard area for the following reasons:

- without detection, the identity of the industrial chemical cannot be determined with certainty;

- without monitoring, the concentration of the industrial chemical cannot be determined, and

- without monitoring, the concentration of oxygen cannot be determined.

The ACE Directive further stated that, "Self-contained breathing apparatus (SCBA) is the protection of choice when individuals (usually reconnaissance or rescue personnel) must operate inside or in the proximity of a TICs hazard."

In a normal operational situation all forces would have military respirators, whereas very few would have self-contained breathing apparatus. Consequently, it is necessary to know the level of protection provided by the military respirators in the event that the force cannot immediately evacuate the hazard zone.

The Canadian Forces are equipped with the C4 mask and the C7 canister. A detailed description of the C7 canister and its performance is given in reference 3. The C7 plastic canister is the first Western canister to provide protection against the full spectrum of chemical warfare (CW) agents, including blood agents (e.g., hydrogen cyanide (AC), cyanogen chloride (CK)), nerve agents (e.g., sarin (GB), soman (GD), VX), mustard and organofluorine penetrants (e.g.,

perfluoroisobutene (PFIB)). Like its predecessor, the metal-body C2 canister, the C7 canister also provides varying degrees of protection against a variety TICs.

The present report describes the determination of the gas-life of the C7 canister against chlorine at different concentrations and humidities. This information coupled with estimations of the chlorine concentration, calculated for accidental releases using the CANSLAB heavy gas model, is then used to provide guidance for the safe use of the gas mask canister ensemble against chlorine challenges.

## 2.0    EXPERIMENTAL

References 3-7 define the minimum protection level which should be provided by the adsorbent (impregnated carbon in this case) inside the C7 canister against a list of representative toxic chemicals. Since the C7 canister was developed for military use by the Canadian Forces (CF), chemical warfare agents such as CK, AC or dimethylmethylphosphonate (DMMP), a simulant for GB, are used in standard protection level determinations. The protection level is represented by gas-life, or breakthrough time. For any given chemical, the gas-life of the canister is the time it takes to reach a pre-determined breakthrough concentration when challenged at some initial concentration (usually 4,000 $mg.m^{-3}$ for CW agents). The breakthrough concentration is usually the level at which physiological effects appears, and is thus a function of the gas (e.g., 1 ppm for AC and 1 ppm for CK [6]).

The protection level afforded by the C7 canister for chlorine was determined by a series of experiments using initial chlorine levels ranging from 1,000 to 10,000 ppm and a breakthrough concentration of 0.5 ppm. The challenge levels reflects the concentration range expected from small to moderate releases of chlorine. The breakthrough concentration is one-half the concentration that can be sensed by the human nose (1 ppm) and one-twentieth of that considered immediately dangerous to life and health (IDLH) [8]. Thus, the criteria selected for the determination are very conservative.

## 2.1    Chlorine Challenge Experiments

Racal Filter Technologies Inc. (RFTI), Brockville, Ontario, performed the chlorine challenge experiments on the C7 canisters.  For completeness of this report, the detailed instruction on the chemicals required, calibration of the chlorine concentrations and the breakthrough measurement employed by RFTI is attached as Annex B.

The chlorine challenges were performed under the following conditions:

| | | |
|---|---|---|
| Inlet Concentration (ppm) | = | 1000, 2500, 5000, 7500 and 10600 |
| Temperature (°C) | = | ambient (23 to 25) |
| Air Flowrate (L/min) | = | 30 |
| Relative Humidity (%) | = | 50 and 80 |
| Breakthrough Concentration (ppm) | = | 0.5 |

## 3.0    MODELLING CHLORINE RELEASES

Toxic industrial chemicals (TICs), such as chlorine, ammonia, and natural gas are stored, transported, handled, and used in large quantities in the form of pressurised liquids.  These TICs, which have critical temperatures above and boiling points below the ambient air temperature, are liquefiable by pressure alone, and in liquid form are referred to as liquefied gases.  TICs of these types are distinguished by their ability to "flash", viz. if containment is lost, these materials will instantly vaporise a fraction of the liquid and cool down to the ambient atmospheric pressure boiling point.  Denser-than-air clouds are formed in many of these types of releases.  Because they can give rise to dangerous vapour clouds, TICs of these types can form a considerable chemical vapour hazard when released into the atmosphere.  To facilitate the evaluation of this hazard, the Defence Research Establishment Suffield (DRES) developed the CANSLAB dense gas model[1].

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1.  Originally, the CANSLAB dispersion model was developed by The Technical Co-operation Panel (TTCP) Chemical and Biological Defence Group Technical Panel 9 (TP-9) to fulfil the US/UK/CA Memorandum of

The CANSLAB model is a similarity model that uses simplified forms of the conservation equations (species, mass, energy, and momentum) that are obtained by averaging the plume properties over a crosswind plane for a continuous release, or the cloud properties over the entire cloud volume for an instantaneous release. The basic conservation laws, along with various submodels, form a set of coupled differential and algebraic equations that describe mathematically the physics of denser-than-air gas dispersion. This theoretical framework is completed by the inclusion of the equation of state (ideal gas law) and the equations for the growth of the cloud dimensions (e.g., plume width in the steady-state plume mode, and puff length and width in the transient puff mode). The CANSLAB model accounts for a number of physical phenomena that do not occur or are unimportant in neutrally buoyant gas releases. These phenomena include:

- gravitational slumping and spreading which is driven by the buoyancy pressure causing the initial cloud to advance characteristically into the surroundings behind a gravity front which tends to produce a wider and lower cloud;

- reduced turbulent mixing due to stable density stratification in the vertical direction;

- self-generated flow set up by the horizontal density differences which introduce a velocity shear at the cloud surface, leading to a gross intermingling of contaminant cloud material with clean air (entrainment of air) and eventually turbulence generation and consequential turbulent mixing and cloud dilution;

- turbulent mixing of the cloud with the ambient atmosphere, which is treated by using the entrainment concept that specifies the rate of air flow into the cloud;

- thermodynamic effects due to aerosol droplet formation and evaporation, which is modelled by using the local thermodynamic equilibrium approximation in which the ratio of liquid to vapour is determined by requiring the partial pressure of the vapour phase to be equal to the saturation vapour pressure until all the liquid droplets are evaporated;

- cloud heating due to temperature differences between the ground and the airborne vapour, which is treated by using the radiation boundary condition and a coefficient of surface heat transfer;

- transition from the dense gas phase to the passive phase as the cloud of dispersing gas gains buoyancy by entraining air and, if the cloud is cold, by absorbing heat from the ground; and,

- the physical effects due to normal atmospheric advection and turbulent diffusion.

In consequence, most of the basic physical phenomena associated with dense gas dispersion are properly accounted for in CANSLAB.

CANSLAB has been designed to simulate the atmospheric dispersion of dense gases resulting from the release of TICs for a number of different source release conditions: (i) catastrophic (instantaneous) releases (e.g., catastrophic pressure vessel failure); (ii) cryogenic pool spills and subsequent evaporation; (iii) multiphase jets that are released either horizontally or vertically; and (iv) combinations of these individual components, each of which could involve the effects of various physical, chemical, and thermodynamic phenomena on the turbulent diffusion process. Furthermore, CANSLAB incorporates a comprehensive, integrated dispersion modeling environment with an intuitive "point-and-click" interface that provides an efficient and powerful tool for military planning and hazard assessment. The model maintains a database of common TICs that contains information on the physical, chemical, and toxicological properties required for the simulation and subsequent hazard assessment. Finally, the model incorporates extensive graphical facilities for data analysis and display either at a workstation (or personal computer) or as hardcopy of all intermediate and final model results. Graphical displays of model outputs include:

- line plots of all variables (e.g., cloud size; cloud temperature, density, and composition; transport velocity of the cloud; entrainment velocities; etc.) involved in the dispersion process;

- concentration-time histories at any receptor location downwind of the release; and,

- site plans showing the cumulative dosage, toxic load, probit function, and probability of lethality isopleths.

## 4.0 RESULTS AND DISCUSSIONS

### 4.1 Chlorine Breakthrough Times

Table 1 summarizes the breakthrough times obtained from the chlorine challenge experiments. The log-log plots of Canister Breakthrough Times versus Chlorine Challenge Concentration at the two relative humidities are shown in Figures 1 and 2.

**Table 1**

**Chlorine Breakthrough Times for C7 Canisters**

| Concentration (ppm) | Breakthrough Times (min) @ 50% RH | Breakthrough Times (min) @ 80% RH |
|---|---|---|
| 1000 | 175 | 165 |
| 2500 | 49 | 61 |
| 5000 | 23 | 25 |
| 7500 | 18 | 21 |
| 10600 | not done | 11* |

* The canister combusted 11 minutes into the challenge

### 4.2 Determination of Ignition and Breakthrough Distances

This study attempts to determine "safe" distances for masked personnel exposed to vapour resulting from the catastrophic release of chlorine. To determine these distances, a number of source conditions involving the catastrophic release of pressurised vessels of chlorine have been modelled with CANSLAB, and the resulting challenge levels compared with the protection levels afforded by the Canadian C7 canister.

The purpose of the chlorine gas challenge experiments on the C7 canister was to define all sets of exposure conditions (i.e., the challenge concentration and exposure duration) that will lead to a breakthrough of the canister. The objective of the modelling effort was to derive a quantitative prediction of protection levels afforded by the C7 canister against chlorine. The requirement for the quantification of the protection levels provided by the C7 canister against chlorine can be satisfied most easily by developing a simple functional relationship between the challenge concentration, $C$, and the exposure time, $t$, that results in breakthrough of the canister, such that the end-product of the relationship is a constant numerical value, viz.

$$f(C, t) \equiv B \,, \tag{1}$$

where $B$ is a constant in the appropriate units. The form of this equation and the units of the constant will vary according to the material used for the canister challenge experiments. For chlorine, the challenge experiments on the C7 canister that are summarized in Table 1 suggest that the breakthrough condition can be modeled adequately using the following relationship:

$$f(C, t) \equiv Ct = B = 148000 \ \text{ppm.min} \,. \tag{2}$$

The adequacy of this relationship for modelling the breakthrough condition of chlorine against the C7 canister is shown in Figures 1 and 2. These figures show a simple (log-log) plot of the breakthrough time [$\log(t)$] against the challenge concentration [$\log(C)$] for the data summarised in Table 1 (i.e., at the two relative humidities) superimposed on the theoretical prediction provided by Equation (2). The slope of the linearly regressed line has been round off to 148000 ppm-min. Note that the empirical relationship in Equation (2) agrees well with the measurements of the breakthrough times at the two relative humidities tested. This means that the breakthrough on the C7 canister is not humidity-dependent, and the data collected for both humidities could be grouped together.

The $Ct$ relationship of Equation (2) defines the breakthrough condition for chlorine challenges of the C7 canister and, as such, corresponds to one critical endpoint of the protection afforded by the canister. A second critical endpoint in the protection level afforded by the C7 canister against chlorine concerns the fact that the canister is known to spontaneously ignite when the challenge

chlorine concentration exceeds 10000 ppm. Hence, both critical endpoints must be considered in any risk analysis involving the protection afforded by the C7 canister against various chlorine challenges.

Certainly, it could be argued that the C7 canister may have ignited at much lower challenge concentration (below 10000 ppm). There is insufficient data in Table 1 to suggest that 10000 ppm is the "magic number", or in any way validating the claim. These results were not duplicated because it was felt that the chlorine challenge experiments are too dangerous to be repeated at concentrations above 7500 ppm. In addition, the chlorine challenge at 10600 ppm lasted 11 minutes before ignition was observed. Thus, it was felt that 10000 ppm is a conservative estimate of the "ceiling ignition concentration".

In order to examine the implications of the protection levels afforded by the C7 canister as delineated by the two critical endpoints enunciated above (i.e., the breakthrough condition summarised by Equation (2) and the combustion condition), these endpoints were used in conjunction with one particular dense gas dispersion model CANSLAB. This allows a close examination of the results obtainable for a given set of notional releases of chlorine under one type of atmospheric condition at two different ambient temperatures.

To that end, we consider a single release scenario, namely, that of a catastrophic or instantaneous release of $Q$ kg of chlorine representing notional catastrophic failures of fully pressurised vessels of chlorine. Runs were made with 1, 10, 100, 200, 300, 400, and 500 metric tonnes (i.e., $Q =$ 1000, 10000, 100000, 200000, 300000, 400000, and 500000 kg) as the quantity released. To place these quantities of chlorine in perspective, it is noted that chlorine is routinely shipped in one ton cylinders and that one railway tanker car nominally can hold about 90 tons of liquefied chlorine. In all the simulations, the atmospheric condition was assumed to correspond to stable stratification (i.e., Pasquill Stability Category E) with a windspeed of 2 m.s$^{-1}$ at 2-m height, which corresponds to a credible but worst case outcome. Runs were made for two different initial temperatures of the superheated pressurised liquid chlorine, namely at 25°C and 35°C, which correspond, respectively, to 59.5 and 69.5 degrees of superheat (i.e., the atmospheric pressure

boiling point of chlorine is -34.5°C). In all these runs, it has been assumed that some of the liquefied chlorine becomes airborne as a mixture of aerosol droplets and vapour. The partition between vapour and liquid is determined by the thermodynamic vapour flash fraction, $f_v$. The vapour flash fraction is calculated by assuming that the heat required to evaporate that quantity of vapour is supplied by cooling of the whole of the initially liquid quantity in the tanker car from its storage temperature down to the atmospheric pressure boiling point temperature. Hence, the flashing fraction is estimated from the relationship:

$$f_v = 1 - \exp\left(\frac{-c_{p,l}(T - T_{b.p.})}{\Delta H}\right) , \tag{3}$$

where $c_{p,l}$ is the specific heat of the liquid chlorine, $T$ is the ambient (storage) temperature, $T_{b.p.}$ is the boiling point temperature of chlorine at atmospheric pressure, and $\bullet H$ is the heat of vaporisation of chlorine at the boiling point temperature. It is assumed that $f_v(1 - f_v)$ of the fraction of the material in the liquid state after the initial flash is present in the form of liquid aerosol droplets in the chlorine cloud.

As the chlorine cloud formed from the initial "flash" advects downwind, its size increases while the concentration is decreased due to turbulent mixing, so that at each point downwind along the cloud centerline there corresponds a sequence of $C(t)$ and $t$ pairs whose integrated effects yield a total dosage,

$$D \equiv \int_0^\infty C(t)dt , \tag{4}$$

obtained from the passage of the entire cloud over the receptor location. The total dosage at each receptor location along the cloud centerline can be compared with the breakthrough constant $B$ exhibited in Equation (2), the latter of which defines the breakthrough condition for the C7 canister. The output is a set of cloud centerline dosages, $D$, within which exposures in excess of the breakthrough condition [e.g., $D > B$; cf. Equation (2)] will be experienced, according to the model. The decrease of the centerline dosage, $D$, with downwind distance, $x$, can be used to determine the minimum downwind distance, $x_*$, beyond which canister breakthrough will not

occur when exposed to the passage of the entire cloud arising from the particular release scenario. Mathematically, the determination of $x_*$ requires the solution of the following equation:

$$D(x_*) = B,\tag{5}$$

where $B = 148000$ ppm.min as defined by Equation (2). In practice, the decrease of the cloud centerline dosage, $D$, with downwind distance, $x$, can be modelled by a power-law relationship of the form

$$D(x) = Ax^{-\gamma}, \quad \gamma > 0\tag{6}$$

where $A$ and $\gamma$ are constants that depend implicitly on the atmospheric conditions and the source mass. Equations (5) and (6) imply that the minimum breakthrough distance $x_*$ can be determined from

$$x_* = \left(\frac{B}{A}\right)^{-1/\gamma}.\tag{7}$$

Similarly, the minimum downwind distance, $x_{**}$, beyond which the C7 canister will not spontaneously ignite is determined from the condition

$$C_0(x_{**}) = C_* \equiv 10000 \ \text{ppm},\tag{8}$$

where $C_0(x)$ denotes the peak mean concentration at downwind distance $x$ (e.g., this corresponds to the cloud centerline mean concentration at downwind distance $x$). Also, it is known that the decrease of the peak mean concentration with $x$ can be modelled by a power-law form

$$C_0(x) = K x^{-\tau}, \quad \tau > 0\tag{9}$$

where $K$ and $\tau$ are constants. Combining Equations (8) and (9) implies that the minimum ignition distance $x_{**}$ can be determined from

$$x_{**} = \left(\frac{C^*}{K}\right)^{-1/\tau} . \qquad (10)$$

The decrease of the peak mean concentration, $C_0$ and total dosage, $D$, with downwind distance $x$ predicted by CANSLAB, is shown in Figures 3 to 9 for the simulations conducted at 25°C for releases of 1000, 10000, 100000, 200000, 300000, 400000, and 500000 kg of chlorine, respectively. The power-law decays of $C_0$ and $D$ with $x$ are clearly demonstrated in these figures. The power-law forms exhibited in Equations (9) and (6) were fitted, respectively, to the peak mean concentration and total dosage data presented in Figures 3 to 9. The results of these least-squares fits are summarised in Tables 2 and 3 for the runs conducted at 25 and 35°C, respectively.

### Table 2

### Simulated Peak Mean Concentration, $C_0$, and the Total Dosage, $D$ at 25°C

| $Q$ (kg) | $K$ (ppm.m$^\tau$) | $\tau$ | A (ppm.min m$^\gamma$) | $\gamma$ |
|---|---|---|---|---|
| 1,000 | $3.07 \times 10^7$ | 1.78 | $1.21 \times 10^6$ | 1.09 |
| 10,000 | $2.93 \times 10^8$ | 1.88 | $2.52 \times 10^7$ | 1.35 |
| 100,000 | $5.04 \times 10^9$ | 2.00 | $2.98 \times 10^8$ | 1.40 |
| 200,000 | $5.04 \times 10^9$ | 1.96 | $6.49 \times 10^8$ | 1.43 |
| 300,000 | $8.37 \times 10^9$ | 1.99 | $1.08 \times 10^9$ | 1.45 |
| 400,000 | $1.03 \times 10^{10}$ | 1.98 | $1.24 \times 10^9$ | 1.43 |
| 500,000 | $1.16 \times 10^{10}$ | 1.97 | $1.36 \times 10^9$ | 1.41 |

## Table 3

### Simulated Peak Mean Concentration, $C_0$, and the Total Dosage, $D$, at 35°C

| $Q$ (kg) | $K$ (ppm.m$^\tau$) | $\tau$ | A (ppm.min m$^\gamma$) | $\gamma$ |
|---|---|---|---|---|
| 1,000 | $5.59 \times 10^7$ | 1.90 | $1.42 \times 10^6$ | 1.11 |
| 10,000 | $3.69 \times 10^8$ | 1.90 | $4.49 \times 10^7$ | 1.43 |
| 100,000 | $3.64 \times 10^9$ | 1.98 | $5.50 \times 10^7$ | 1.48 |
| 200,000 | $7.02 \times 10^9$ | 1.99 | $9.34 \times 10^8$ | 1.46 |
| 300,000 | $9.59 \times 10^9$ | 1.99 | $1.17 \times 10^9$ | 1.44 |
| 400,000 | $1.13 \times 10^{10}$ | 1.98 | $1.33 \times 10^9$ | 1.41 |
| 500,000 | $1.25 \times 10^{10}$ | 1.97 | $1.43 \times 10^9$ | 1.39 |

The power-law relationships for the decay of $C_0$ and $D$ with $x$, summarised in Tables 2 and 3, allow the determination of the minimum breakthrough and ignition distances in accordance with Equations (7) and (10), respectively. The results of these determinations are plotted in Figures 10 and 11 for the simulations conducted at 25°C and 35°C, respectively. These figures show how the minimum breakthrough and ignition distances vary with quantity, $Q$, of material released. It is seen that our data can be fitted very well by the following relationships:

(i)     breakthrough distance, $x_*$, at 25°C increases with $Q$ as

$$x_* = 0.0492\, Q^{0.728} \; ; \tag{11}$$

(ii)     ignition distance, $x_{**}$, at 25°C increases with $Q$ as

$$x_{**} = 5.24\, Q^{0.412} \; ; \tag{12}$$

(iii)    breakthrough distance, $x_*$, at 35°C increases with $Q$ as

$$x_* = 0.0596 \, Q^{0.722} \; ; \tag{13}$$

and,

(iv)    ignition distance, $x_{**}$, at 35°C increases with $Q$ as

$$x_{**} = 5.32 \, Q^{0.417} \; . \tag{14}$$

The conclusion that can be drawn from a perusal of Figures 10 and 11 is clear and unambiguous. The ignition distance, $x_{**}$, determines the "safe" zones for the use of the C7 canister against a chlorine challenge. Provided that personnel are sufficiently far from the source so that the C7 canister does not spontaneously ignite [the minimum downwind distance beyond which this does not occur are given by Equations (12) and (14) for ambient temperatures of 25°C and 35°C, respectively], then personnel donning the C4 mask with the C7 canister can be assured that there will not be breakthrough of the canister for an exposure duration encompassing the entire passage of the chlorine cloud.

## 5.0    CONCLUSIONS

The C7 canister, when exposed to high chlorine concentration, will suffer spontaneous ignition before breakthrough of the canister occurs. The spontaneous ignition distance, as a function of the quantity released, has been determined for the worst but feasible meteorological conditions (2 m.s$^{-1}$, E stability).

Provided the wearer is beyond the spontaneous ignition distance, the C4 mask and the C7 canister should permit the wearer to safely evacuate the area following the release of chlorine. If the wearer is within the ignition distance, the degree and time of protection is determined by the

quantity of chlorine released, the meteorological conditions during the release, and the distance the wearer is from the release point.

The above conclusion validates the guidance provided by ITF-25 and by the NATO ACE Directive, that the use of any respirator is not recommended when dealing with an industrial chemical release. The respirator can provide limited protection and should be used only to escape the hazard area. Consequently, self-contained breathing apparatus must be used when investigating an industrial chemical release.

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8.      U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health, <u>NIOSH Pocket Guide to Hazardous Chemicals</u>, publication number 94-116, stock number 017-033-00473-1.
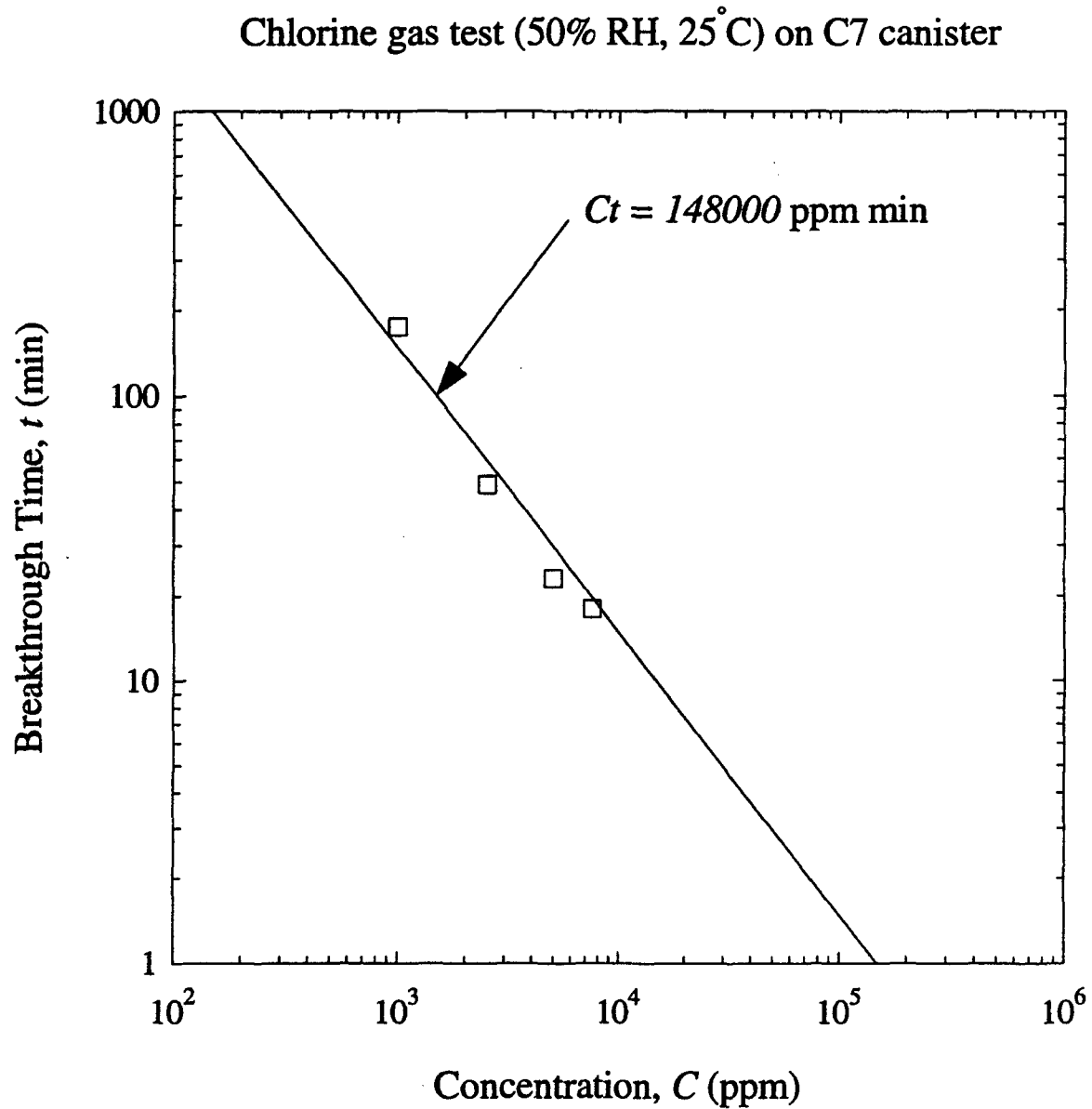
## Chlorine gas test (50% RH, 25°C) on C7 canister



Figure 1        Chlorine Gas Test (50%RH, 25°C) on C7 Canisters
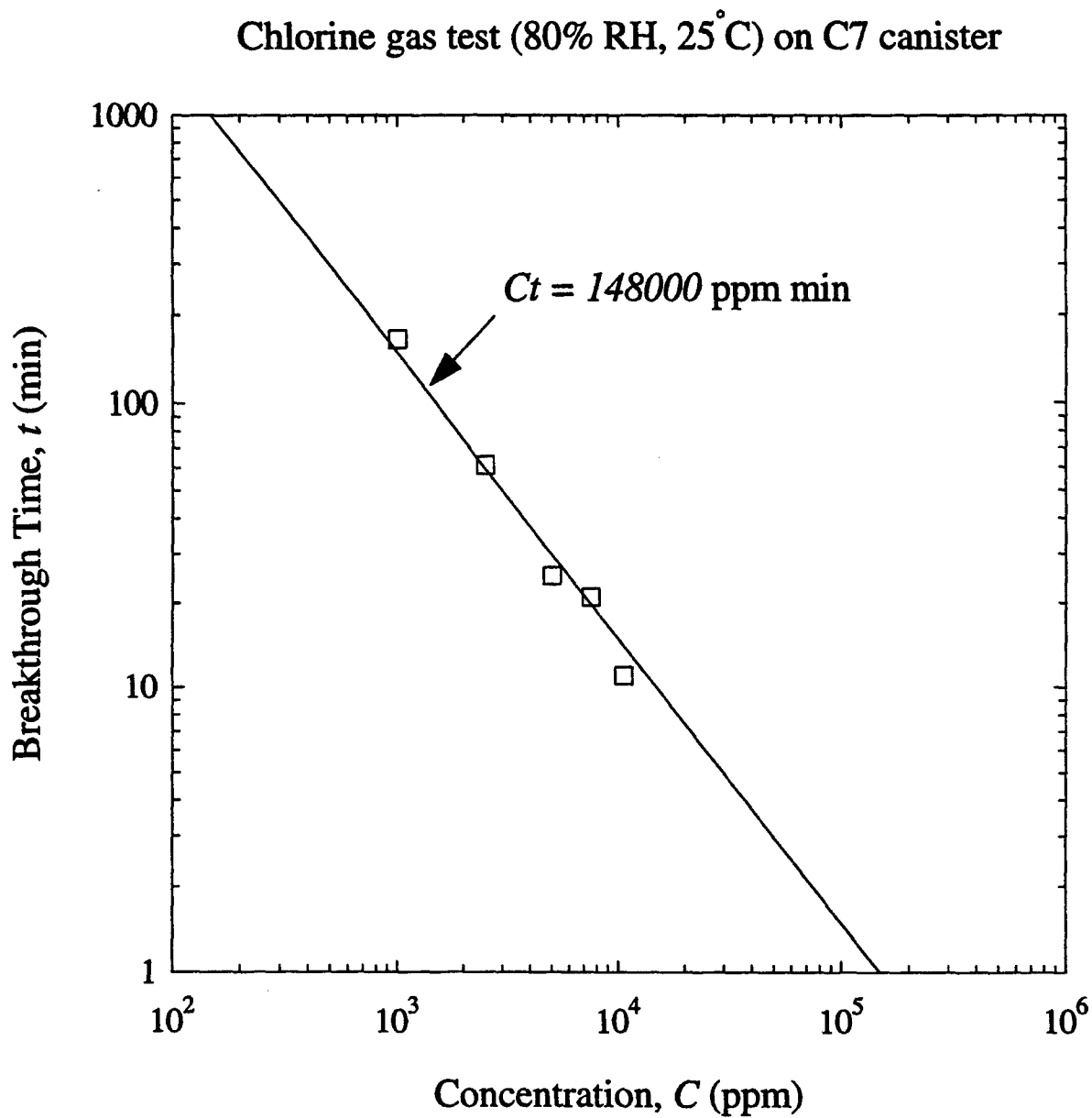
Figure 2    Chlorine Gas Test (80% RH, 25°C) on C7 Canisters
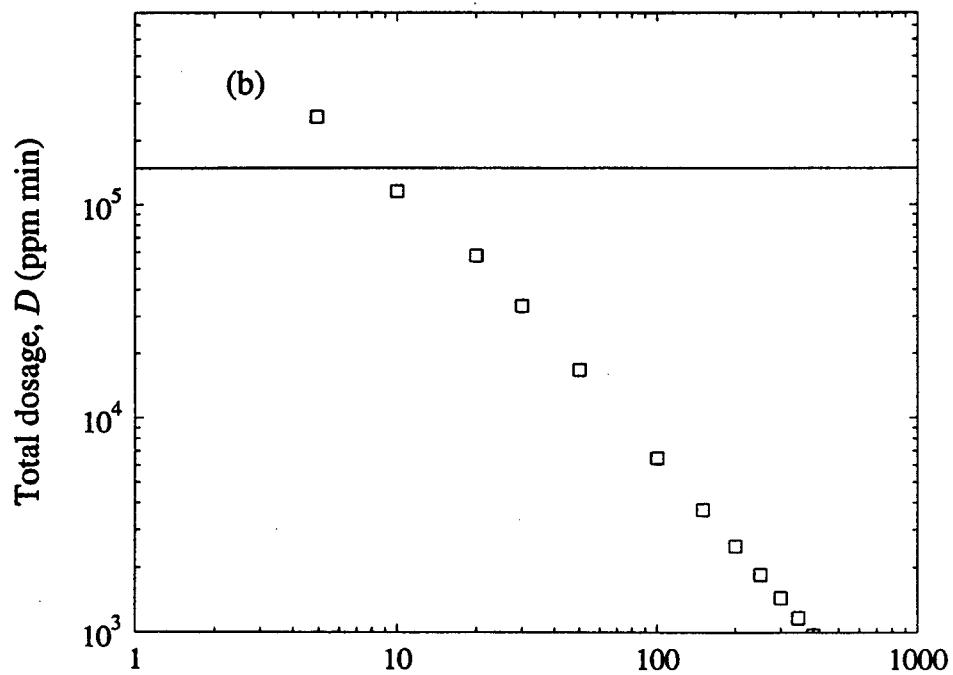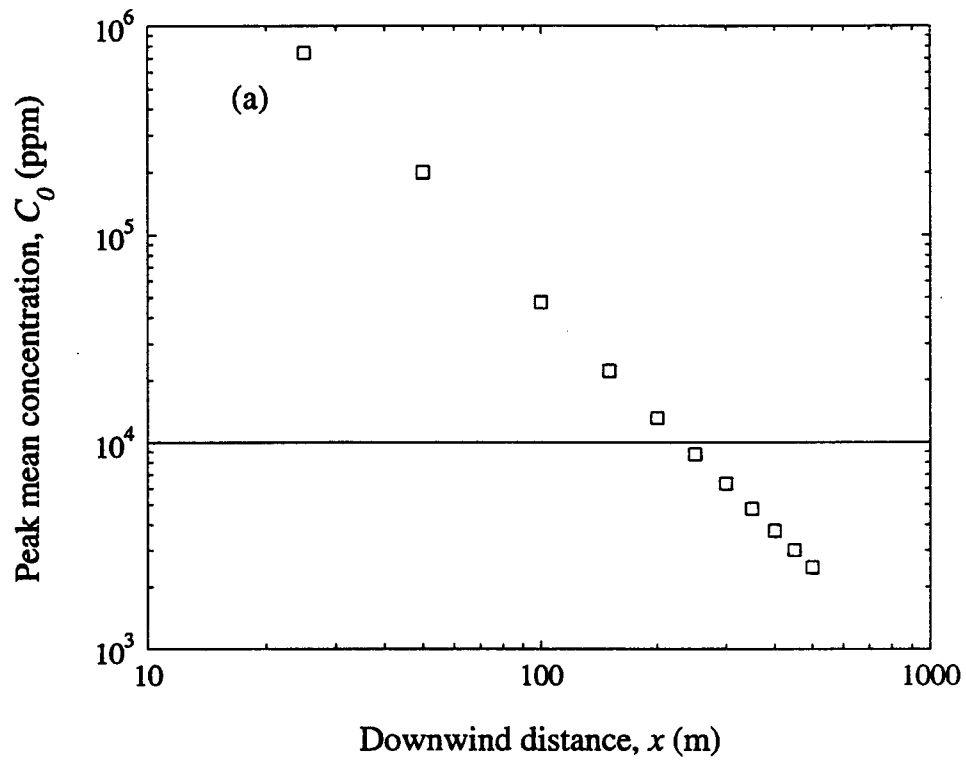
Figure 3          Release of Chlorine Gas (1000 kg)
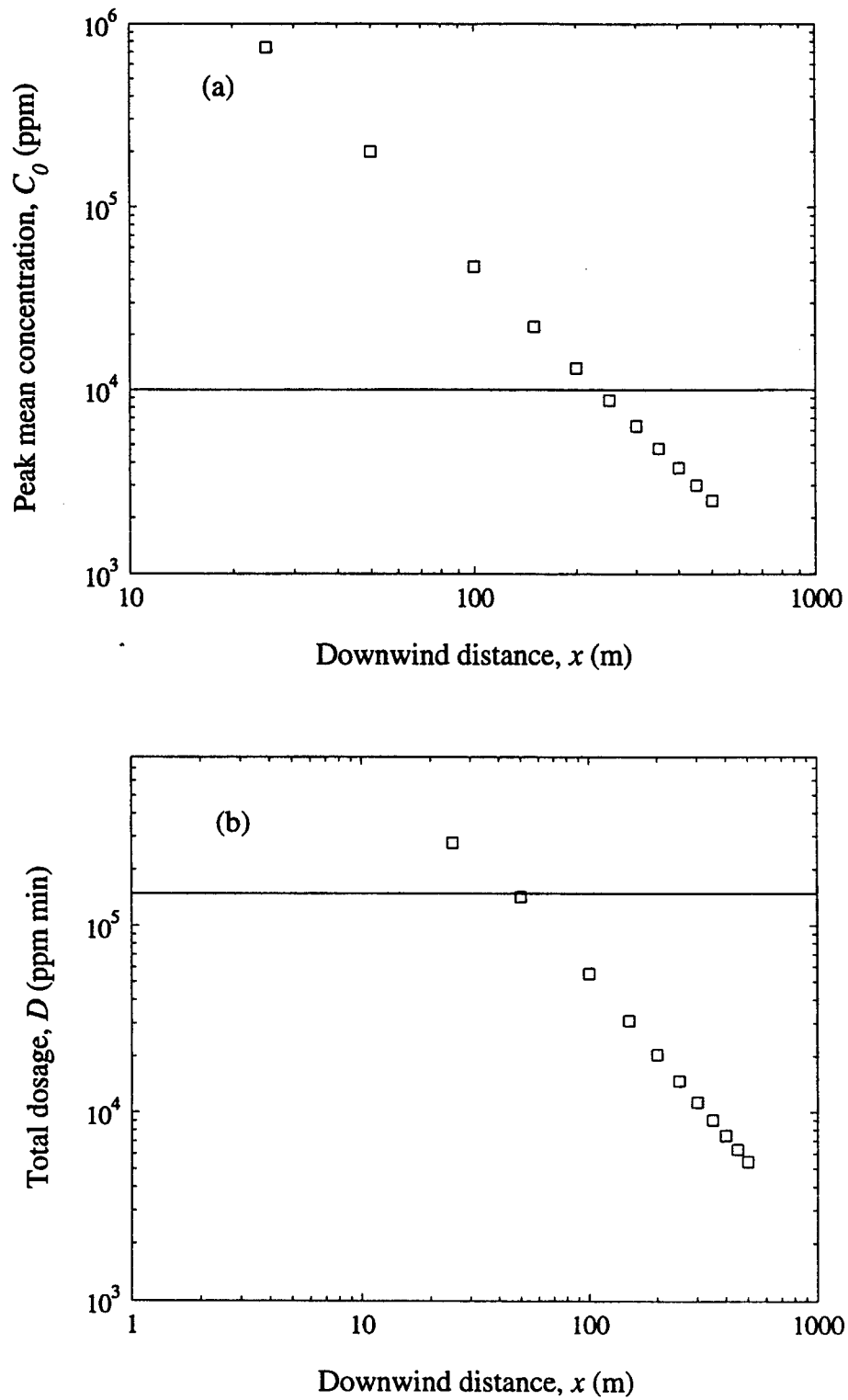
Figure 4       Release of Chlorine Gas (10000 kg)
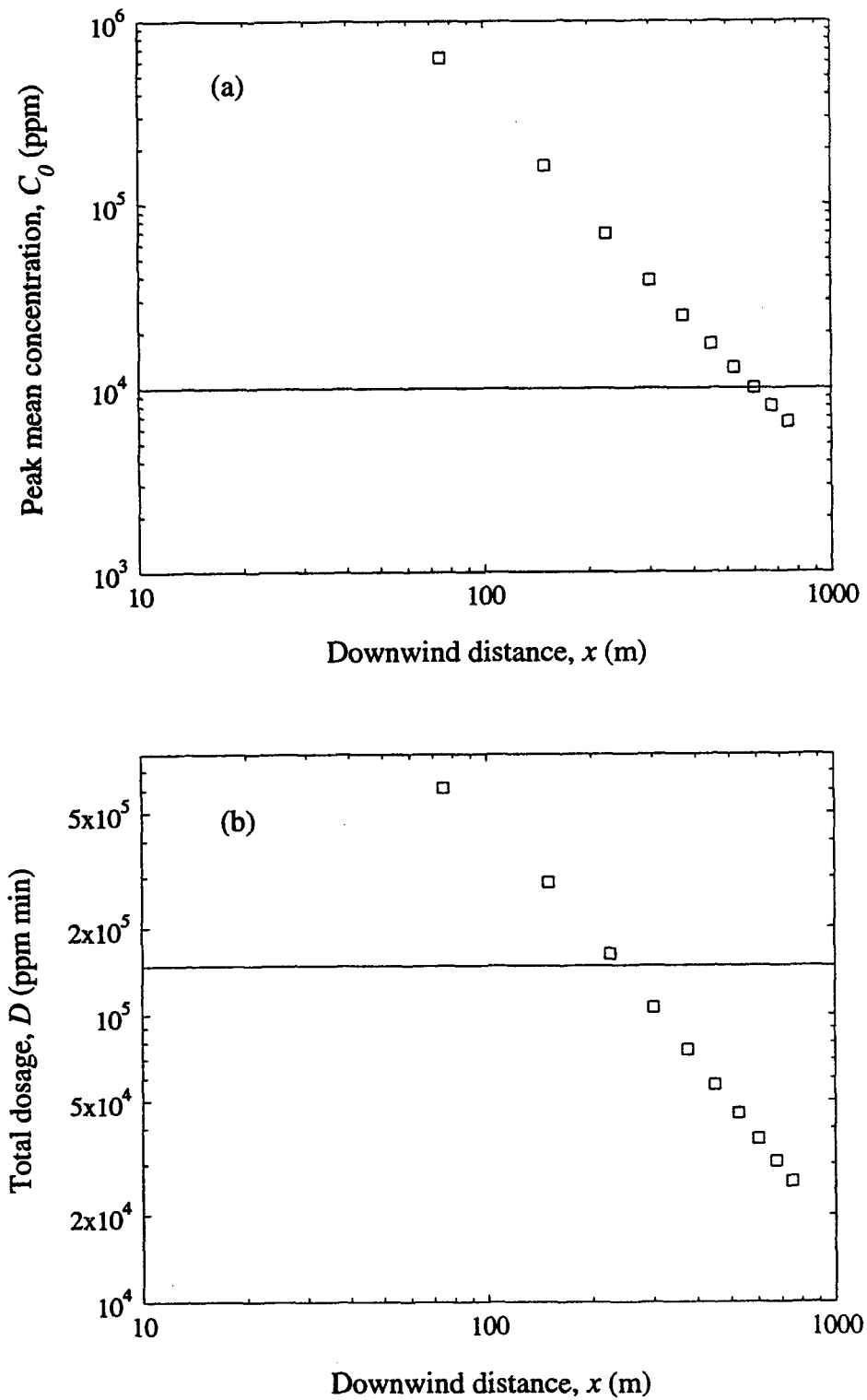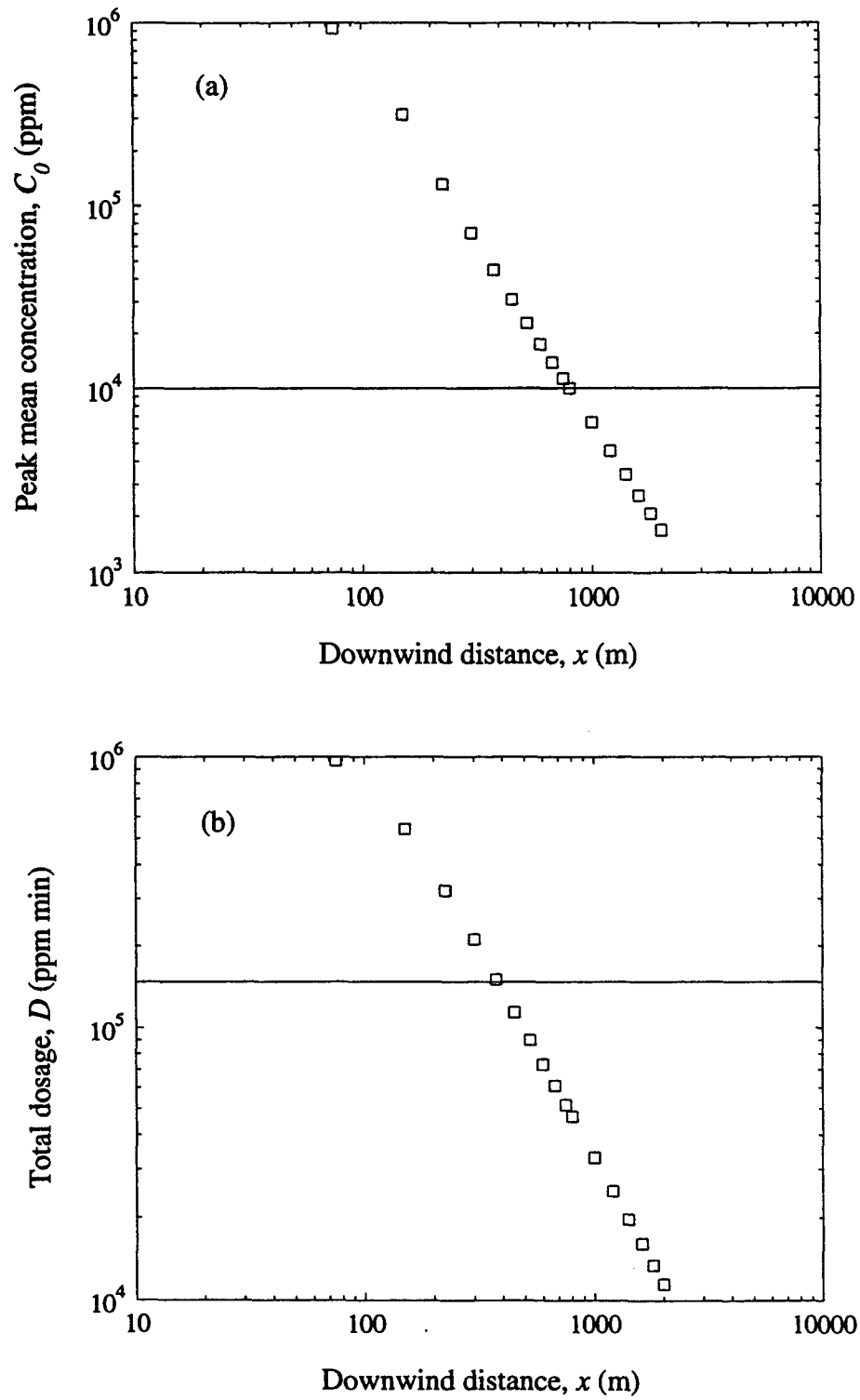
Figure 5    Release of Chlorine Gas (100000 kg)

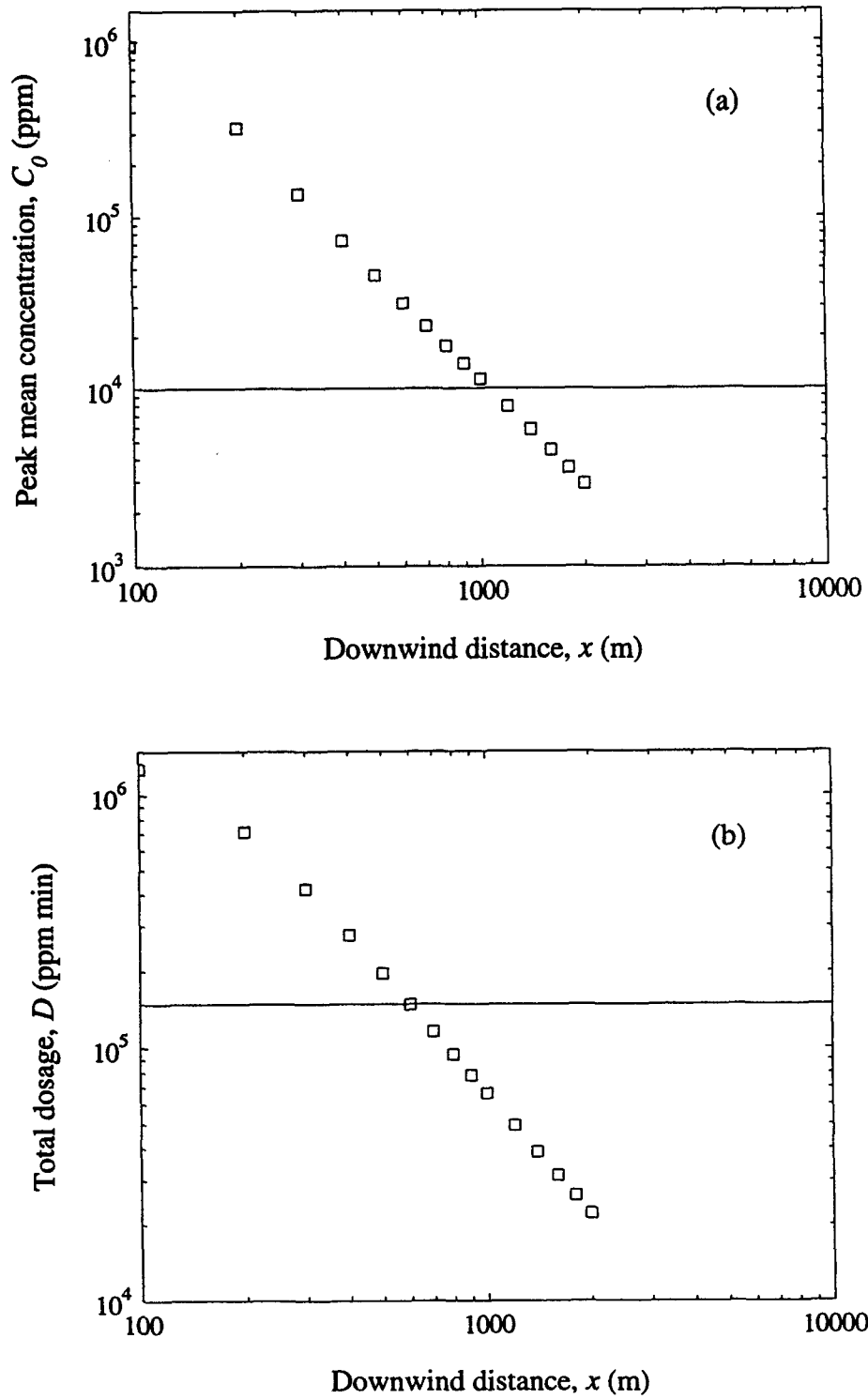Figure 6       Release of Chlorine Gas (200000 kg)
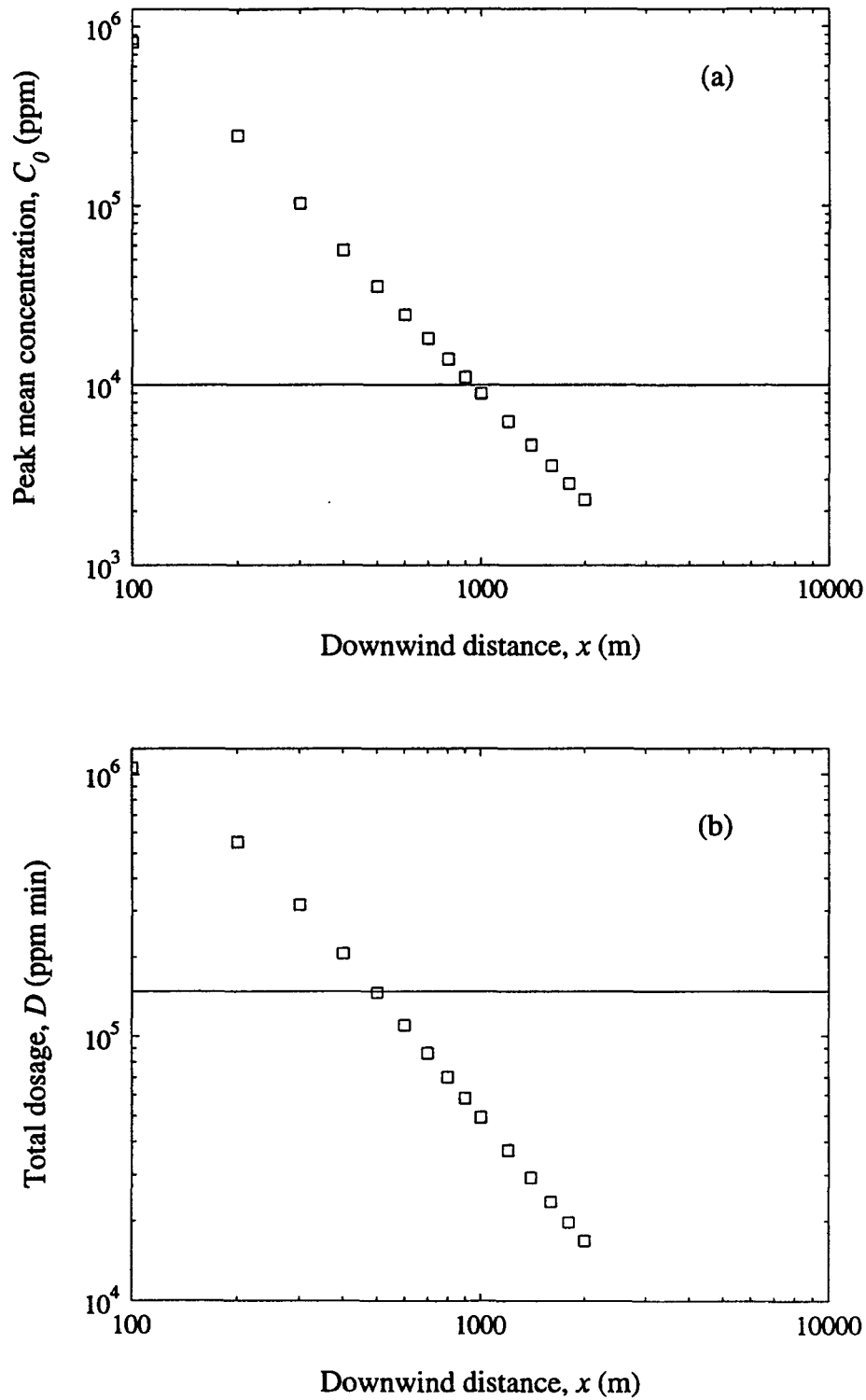
Figure 7        Release of Chlorine Gas (300000 kg)
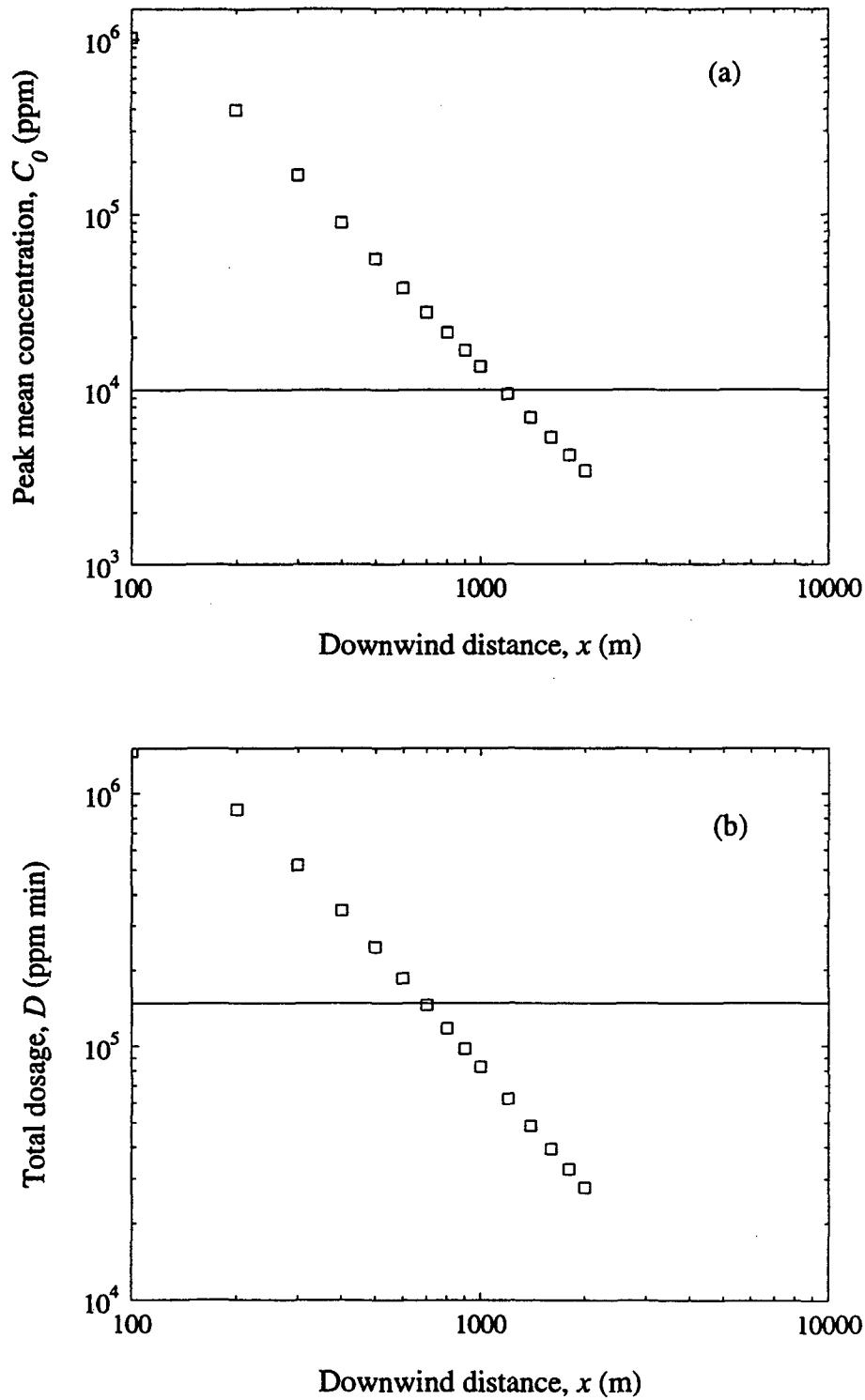
Figure 8        Release of Chlorine Gas (400000 kg)

Figure 9      Release of Chlorine Gas (500000 kg)

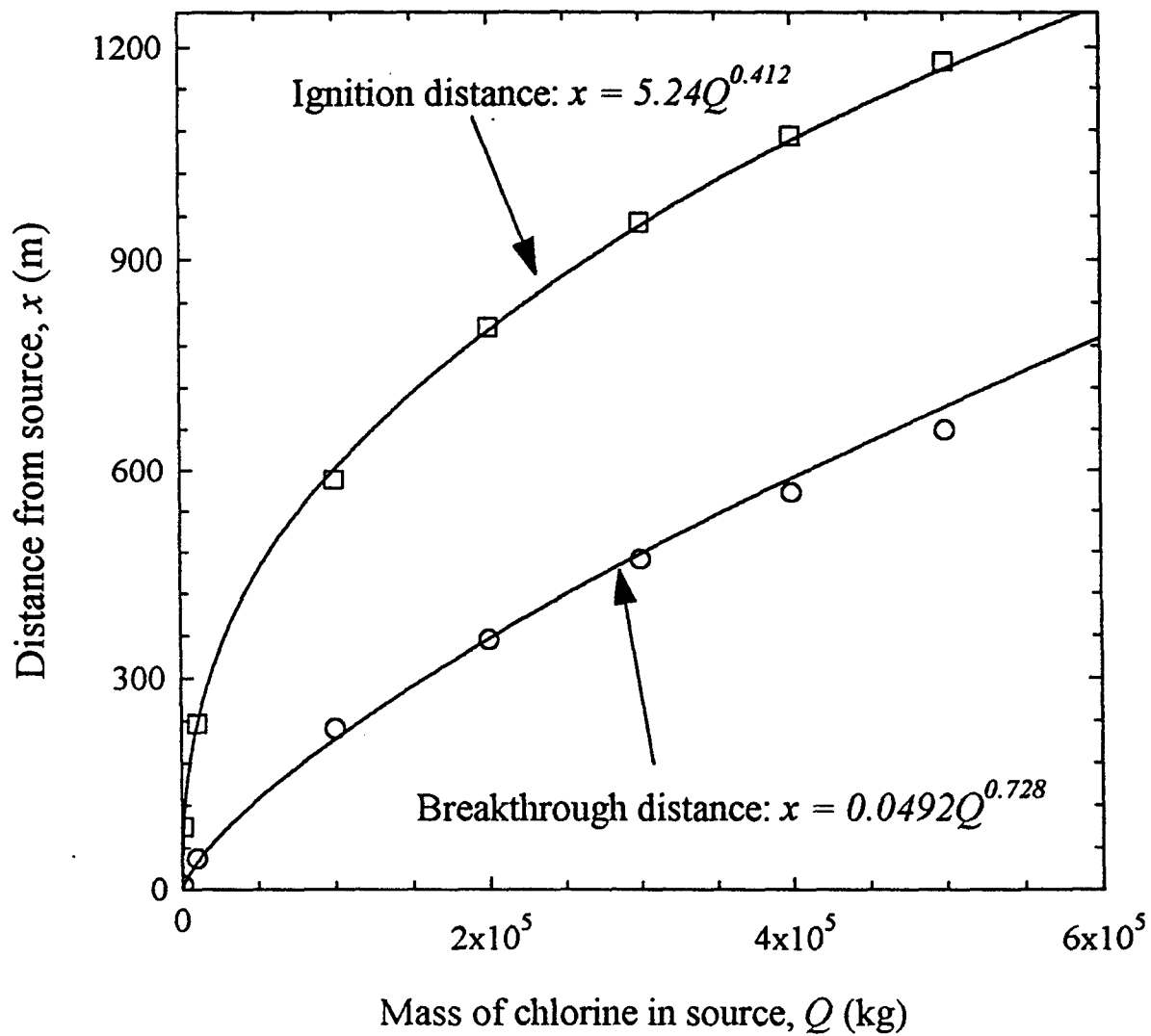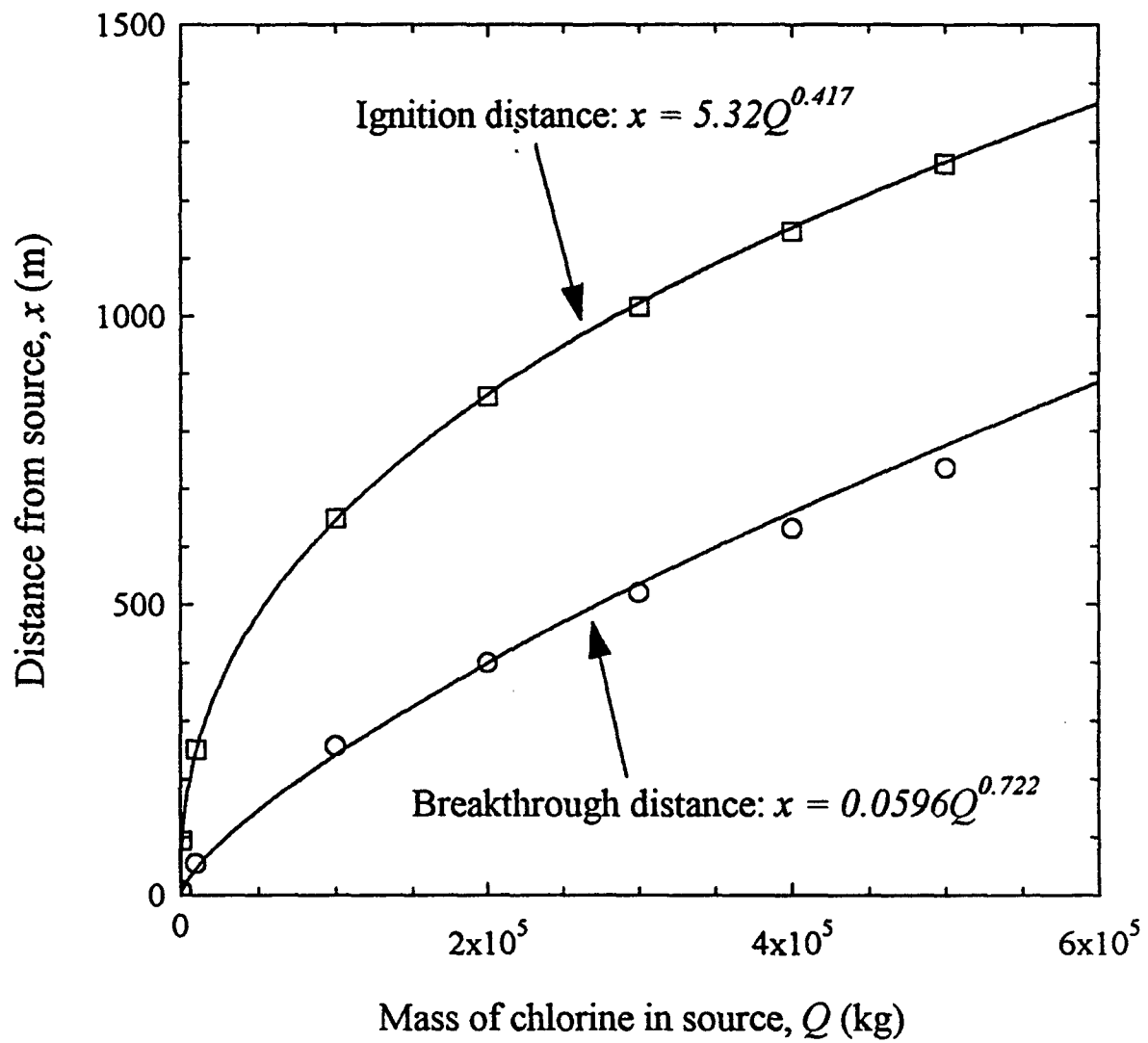Figure 10    Breakthrough and Ignition Distances (80% RH, 25°C)

Ignition distance: $x = 5.32Q^{0.417}$

Breakthrough distance: $x = 0.0596Q^{0.722}$

Figure 11        Breakthrough and Ignition Distances (80%RH, 35°C)

**ANNEX A     ITF-25 HAZARD INDEX RANKING**

| HIGH | MEDIUM | LOW |
|---|---|---|
| Ammonia | acetone cyanohydrin | allyl isothiocyanate |
| Arsine | acrolein | arsenic trichloride |
| boron trichloride | acrylonitrile | bromine |
| boron trifluoride | allyl alcohol | bromine chloride |
| carbon disulfide | allyl amine | bromine pentafluoride |
| chlorine | allyl chlorocarbonate | bromine trifluoride |
| diborane | boron tribromide | carbonyl fluoride |
| ethylene oxide | carbon monoxide | chlorine pentafluoride |
| fluorine | carbonyl sulfide | chlorine trifluoride |
| formaldehyde | chloroacetone | chloroacetaldehyde |
| hydrogen bromide | chloroacetonitrile | chloroacetyl chloride |
| hydrogen chloride | chlorosulfonic acid | cyanogen |
| hydrogen cyanide | crotonaldehyde | diphenylmethane-4'-diisocyanate |
| hydrogen fluoride | diketene | ethyl chloroformate |
| hydrogen sulfide | 1,2-dimethyl hydrazine | ethyl chlorothioformate |
| nitric acid, fuming | dimethyl sulfate | ethylene imine |
| phosgene | ethylene dibromide | ethyl phosphonothioicdichloride |
| phosphorus trichloride | hydrogen selenide | ethyl phosphonous dichloride |
| sulfur dioxide | iron pentacarbonyl | hexachlorocyclopentadiene |
| sulfuric acid | methanesulfonyl chloride | hydrogen iodide |
| tungsten hexafluoride | methyl bromide | isobutyl chloroformate |
| | methyl chloroformate | isopropyl chloroformate |
| | methyl chlorosilane | isopropyl isocyanate |
| | methyl hydrazine | n-butyl chloroformate |
| | methyl isocyanate | nitric oxide |
| | methyl mercaptan | n-propyl chloroformate |
| | n-butyl isocyanate | parathion |
| | nitrogen dioxide | perchloromethyl mercaptan |
| | phosphine | sec-butyl chloroformate |
| | phosphorus oxychloride | sulfuryl fluoride |
| | phosphorus pentafluoride | tert-butyl isocyanate |
| | selenium hexafluoride | tetraethyl lead |
| | silicon tetrafluoride | tetraethyl pyrophosphate |
| | stibine | tetramethyl lead |
| | sulfur trioxide | toluene 2,4-diisocyanate |
| | sulfuryl chloride | toluene 2,6-diisocyanate |
| | tellurium hexafluoride | |
| | tert-octyl mercaptan | |
| | titanium tetrachloride | |
| | trichloroacetyl chloride | |
| | trifluoroacetyl chloride | |

## ANNEX B     CHLORINE GAS TEST

### B1     Materials Required

Chlorine (high purity grade); KI (ACS reagent grade); $Na_2S_2O_3$ (volumetric standard, 0.1 N); $KIO_3$ (ACS reagent grade); Starch Indicator, 1 % (by weight) solution in water.

### B2     Equipment

The set up of the chlorine gas test equipment is shown in Figure B1. This set up is different from that employed at DRES for routine gas testing, but both set ups are functional. The apparatus employed to calibrate the chlorine challenge (inlet) concentration is shown in Figure B2. The outlet (effluent) chlorine concentration may be measured with an Interscan Chlorine Analyzer, or an MDA Continuous Toxic Gas Monitor set at chlorine mode.

### B3     Calibration of Chlorine Challenge Concentration

The bubbler solution is a 2% KI aqueous solution. This solution is prepared by weighing out 10.0 g of KI, adding enough water to bring the volume of the solution to 500.00 mL, mixing the solution well, and then transferring it to a storage bottle.

The $Na_2S_2O_3$ solution is prepared by filling a 50.00 mL pipette with the 0.1 N $Na_2S_2O_3$ volumetric standard solution, draining the pipette into a 200.00 mL volumetric flask, carefully filling the volumetric flask to the mark with distilled water, capping the flask and mixing well. The concentration of the new (diluted) $Na_2S_2O_3$ solution can be calculated by the following:

$$\text{Conc. } Na_2S_2O_3 \text{ (N)} = \text{(Conc. Volumetric Standard (N)} \times 50.00 \text{ mL)}/(200.00 \text{ mL})$$

The $Na_2S_2O_3$ solution is transferred to a storage bottle, capped tightly, and stored in the dark.

The concentration of the prepared $Na_2S_2O_3$ solution may be checked using the following procedure. Place approximately 1.2 g of $KIO_3$ in a glass weighing bottle. Dry this sample in a 120°C oven for approximately 1 hour. Cool the sample to room temperature in a desiccator. Accurately weigh, to ±0.1 mg, the bottle and $KIO_3$. Transfer the $KIO_3$ to a clean, dry beaker and weigh the empty bottle. Dissolve the $KIO_3$ in a minimum amount of distilled water, and transfer the solution to a 1 L volumetric flask. Fill the flask to the mark with distilled water and mix well. Pipette 25.00 mL of this solution into a beaker; add 0.4 g of solid KI and 1 mL of 1 M sulfuric acid. Titrate with the dilute $Na_2S_2O_3$ solution until the solution is a pale yellow colour. Then dilute the solution to approximately 100 mL with distilled water, add 1 mL of starch solution and continue the titration until the blue solution changes to colourless. Repeat with two more 25.00 mL aliquots of the $KIO_3$ solution. The concentration of the $Na_2S_2O_3$ solution can be calculated as follows:

$$\text{Conc. } KIO_3 \text{ (M)} = (\text{Mass } KIO_3 \,/\, (214.00 \text{ , g/mol}))/(1.00 \text{ L})$$
$$\text{Conc. } Na_2S_2O_3 \text{ (M)} = (\text{Conc. } KIO_3 \text{ (M)} \times 25.00 \text{ mL} \times 6)/(\text{ Vol. } Na_2S_2O_3 \text{ (mL)})$$

$$\text{Conc. } Na_2S_2O_3 \text{ (N)} = \text{ Conc. } Na_2S_2O_3 \text{ (M)}$$

The equations for the above reactions are:

$$IO_3^- + 5I^- + 6H^+ \;\rightarrow\; 3I_2 + 3H_2O$$

$$I_2 + 2S_2O_3^{2-} \;\rightarrow\; S_4O_6^{2-} + 2I^-$$
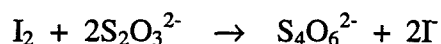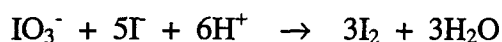
Using a graduated cylinder, fill the bubbler with 50 mL 2% KI solution. Connect bubbler in line between canister test apparatus and wet test meter (as shown in Figure B2). Fit vacuum pump to exit of wet test meter, then turn on the pump. Open chlorine tank and adjust rotameter to the required setting. Allow 3-5 minutes before opening the sample valve. Open the sample valve and permit 1.0 L of air to pass through the bubbler, as indicated on the wet test meter. Close the valve, and record the wet test meter reading. Transfer the solution to a 250 mL beaker and rinse

the bubbler thoroughly with distilled water, collecting all rinsings in the beaker. Titrate with the prepared $Na_2S_2O_3$ solution until the titration solution is a pale yellow colour. Add 5 mL starch indicator solution, and titrate with sodium thiosulfate until the blue colour disappears. The chlorine concentration is the calculated by the following equation:

$$Cl_2 \text{ (ppm)} = \{[(\text{Conc. } S_2O_3^{2-}, N)(\text{Vol. } S_2O_3^{2-}, mL)]/(\text{Vol. Sample, L})\} \times [(24.30 \times 1000)/2]$$

The equations for the above reactions are:

$$2I^- + Cl_2 \rightarrow 2Cl^- + I_2$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$
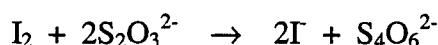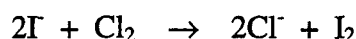
Adjust the gas flow to give the necessary concentration and, if necessary, re-check the concentration. Record the rotameter reading.

## B4    Actual Chlorine Challenge

Ensure that the apparatus is properly assembled as shown in Figure B1, and that there is no canister inside the box. Connect the chlorine gas cylinder with regulator to the rotameter and T-junction (smaller box). The rotameter shall be chosen to give adequate response in the flow rate range required. Leave the chlorine gas off at this stage. Check the molecular sieves in the line from the gas tank. These should be changed every 20 gas tests.

Disconnect the Miller-Nelson unit from the equipment and making sure that the unit is turned off, turn on the water and air supplies. The inlet water pressure must exceed 40 psi and the inlet air pressure must exceed 60 psi. Switch the unit on and set the potentiometers on the front to the required airflow rate, temperature and humidity.

Let the Miller-Nelson unit stabilize for at least 15 minutes.  Using a dry-test meter, measure the airflow.  If necessary, adjust the potentiometer on the front of the unit to give the required airflow, as measured by the dry-test meter.

Use a wet-dry hygrometer to set the temperature and the relative humidity, again setting the Miller-Nelson unit to give these required values, as determined by the hygrometer.  Allow the Miller-Nelson unit to stabilize for 5 minutes, and then connect the outlet hose to the test assembly.

Switch the purge tap to permit nitrogen flow through the system, and install the test canister in the box.  Lower the lid onto the box.  Fit a second (scrub) canister at the box outlet.  Turn on the detector and start chart recorder.  Turn the purge tap again to start flow of chlorine gas, and start timer simultaneously.  Note start point on the recorder trace.  Continue the passage of chlorine gas through the apparatus until the detector indicates that the breakthrough concentration has been reached (0.5 ppm in this case).  Note this time, and other test details and stop the test by switching the purge tap back to allow nitrogen flow, and clearing the test lines for a short time.
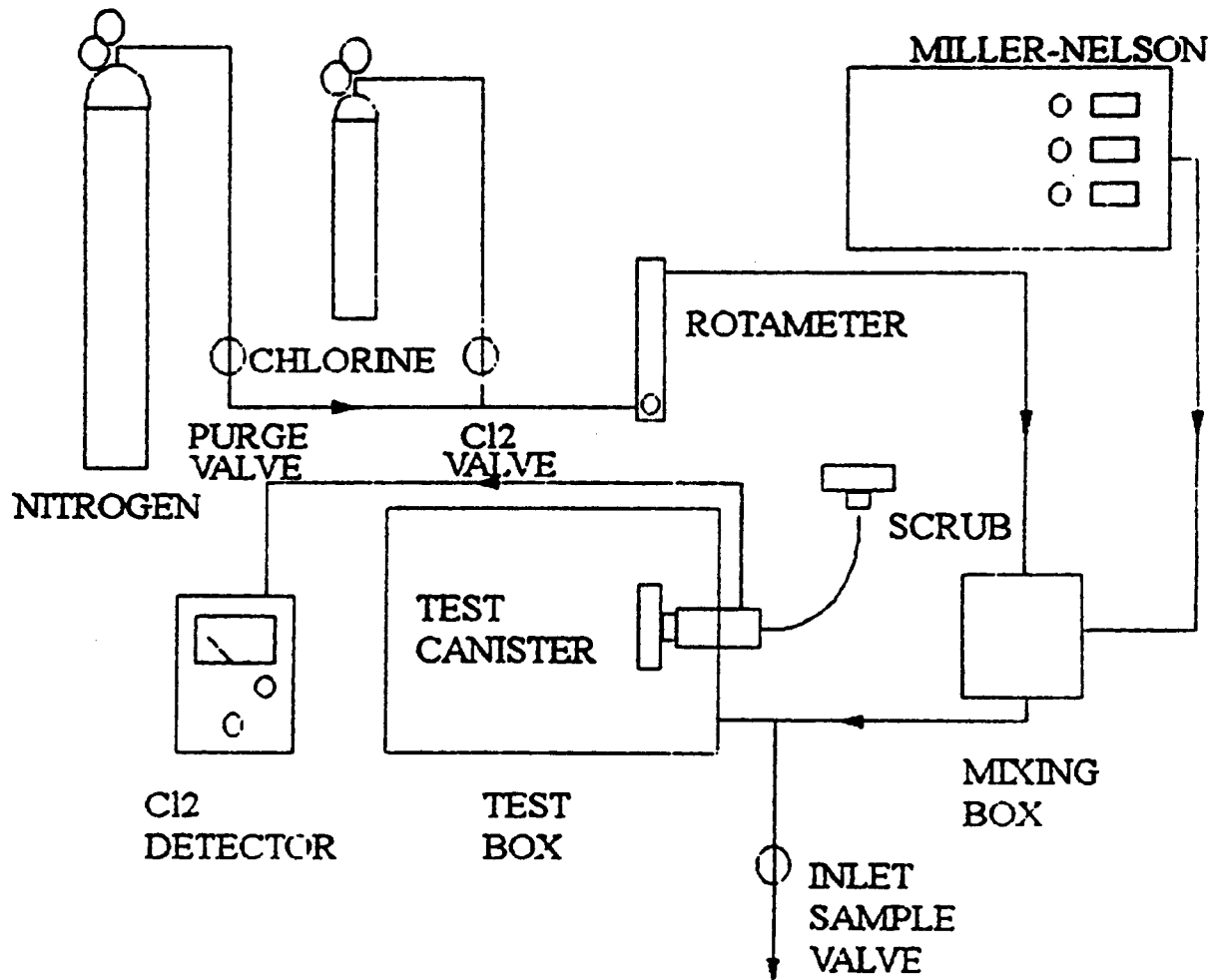
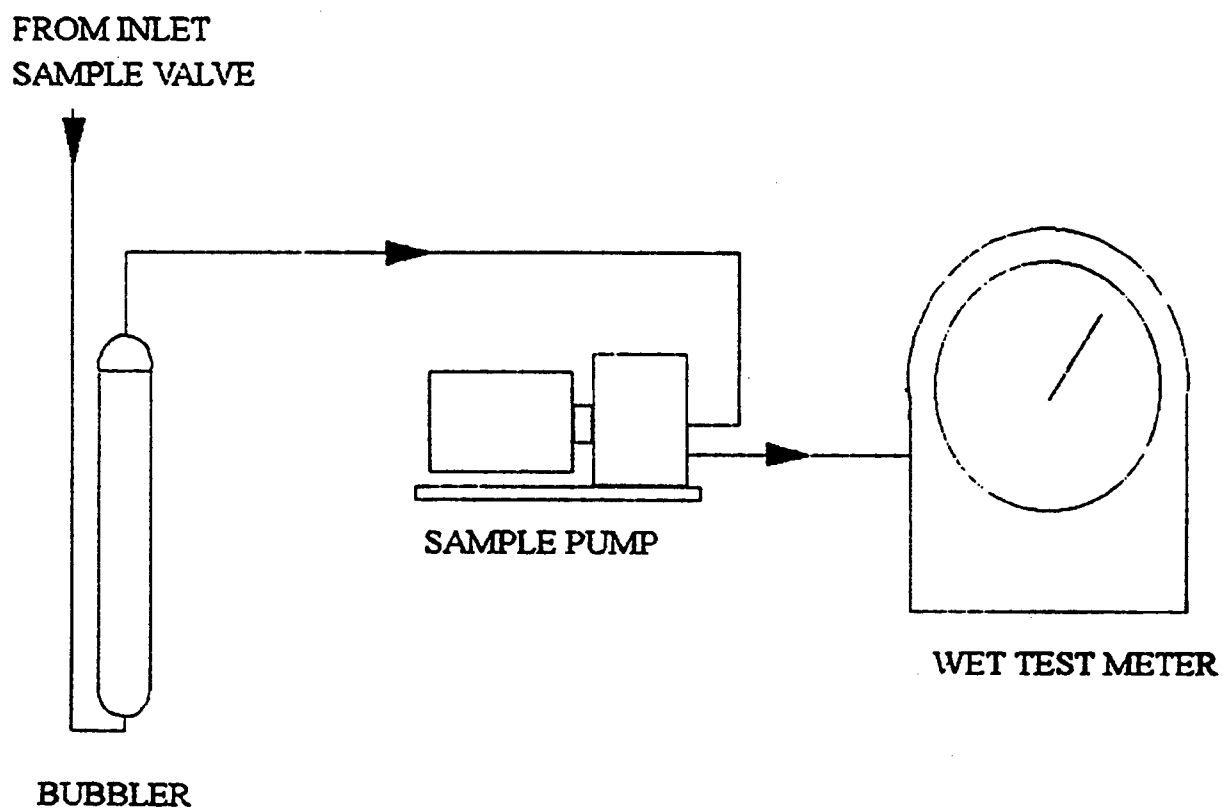Figure B1      Chlorine Test Apparatus

FROM INLET
SAMPLE VALVE

SAMPLE PUMP

WET TEST METER

BUBBLER

Figure B2    Challenge Concentration Measurement Assembly

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Protection Level Afforded by the Canadian C7 Canister Against Single Large-Scale Release of Chlorine

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Liang, S.H.C., Yee, E.C. and Armour, S.J.

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The Canadian C7 canister was challenged at various concentrations of chlorine to determine the breakthrough times. During the breakthrough experiments, it was found that at chlorine concentration above 10,000 ppm, the canister underwent spontaneous ignition before breakthrough occurred. The CANSLAB dense gas model developed at DRES was used to calculate the peak mean concentration and total dosage as a function of downwind distance that can be expected from the catastrophic failure of chlorine cylinders and tank cars under the worst but feasible meteorological condition. Combining the CANSLAB calculations and the breakthrough results, distances downwind of the release site where the C7 canister will ignite (spontaneous ignition distance) or allow breakthrough of chlorine (breakthrough distance) were determined. From the combined result, it could be concluded that providing the wearer is beyond the spontaneous ignition distance, the C7 canister should provide the wearer with respiratory protection and to safely evacuate from an area contaminated with chlorine.

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C7 Canister

CANSLAB dense gas model

Breakthrough Distance

Spontaneous Ignition Distance